DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]In this invention, it is related with the lamination type ceramic electronic component obtained by the manufacturing method and this manufacturing method of the ceramic electronic component obtained by the manufacturing method and this manufacturing method of the ceramic electronic component, and the lamination type ceramic electronic component.

Therefore, it is related with the improvement for heightening the junction power of the ceramic part and conductor film in a ceramic electronic component or a lamination type ceramic electronic component especially.

[0002]

[Description of the Prior Art]For example, when manufacturing a lamination type ceramic electronic component like a multilayered ceramic substrate, the process of forming a conductor film on a ceramic green sheet is carried out. Typically in formation of such a conductor film, the method of using conductive paste or the method of using a metallic foil is adopted.

[0003]However, although these two methods have an advantage, they have the issue by which all should be solved, respectively.

[0004]

[Problem(s) to be Solved by the Invention]In a baking process according to the method of using conductive paste, the glass component contained in each of conductive paste and a ceramic green sheet, Between the metal particles between the ceramic particles in a ceramic green sheet, and in conductive paste, get wet, respectively, spread and anchor structure is formed, The conductor film given with conductive paste can be firmly joined to the ceramic layer to which it was given with the ceramic green sheet.

[0005]However, the conductor film formed with conductive paste does not give a completely precise organization after calcination. It is because the volume of the part in which the organic component contained in conductive paste was burned down serves as a cave and this cave is not thoroughly buried by sintering of metal particles. Therefore, while the lamination of a conductor film and low temperature-ization of calcination temperature are called for in recent years, it is becoming difficult to secure the reliability of a conductor film.
[0006]On the other hand, according to the method of using a metallic foil, since it has a precise structure from before calcination, the lamination of the conductor film formed of this is easy. The surface of a conductor film can be made smoother than the conductor film by conductive paste. Since dispersion of the signal by surface roughness or an internal defect becomes dominant in the high frequency more than a millimeter wave, also in this point, the metallic foil is advantageous.
[0007]When using a metallic foil, etching is typically applied for the patterning, but according to patterning by such etching, compared with the case where screen-stencil of the conductive paste mentioned above is applied, a minute pattern is easily producible.
[0008]Although there is the method of forming a metallic foil as a formation method of a metallic foil according to thin film processes which form a metallic foil with plating on a carrier film, such as a method and sputtering, the method by plating is mainly industrially used from the field of a manufacturing cost.
[0009]However, there is a problem that the bonding strength between a conductor film and ceramics is low in the method of forming a conductor film with a metallic foil.
[0010]Generally the role with a big glass component is played in junction to a conductor film and ceramics about this bonding strength. In the method of using the conductive paste mentioned above, a glass component gets wet and spreads between ceramic particles and between metal particles, forms anchor structure, and joins both firmly. An oxide acts so that a chemical bond with glass may raise bonding strength, while raising wettability with glass. Therefore, in addition to glass frit, an oxide may be added by conductive paste.
[0011]However, since it is very difficult to deposit an oxide with such plating and the conductor film obtained by plating is precise when it is going to form a metallic foil with plating, as mentioned above, it does not have the space where a glass component may permeate.
[0012]Since it is such, it is not so easy to raise the bonding strength of the conductor film and ceramics by a metallic foil.
[0013]Although above-mentioned explanation was performed about a lamination type ceramic electronic component like a multilayered ceramic substrate, the same problem encounters also in ceramic electronic components other than a lamination type ceramic electronic component which have the structure where the conductor film was formed on ceramic element assemblies.

[0014]Then, the purpose of this invention is to provide the ceramic electronic component obtained by each manufacturing method and these manufacturing methods of the ceramic electronic component and lamination type ceramic electronic component which can solve a problem which was mentioned above, and a lamination type ceramic electronic component.
[0015]
[Means for Solving the Problem]This invention is first turned to a manufacturing method of a ceramic electronic component. ******** is characterized by a manufacturing method of ** comprising the following, in order to solve a technical technical problem mentioned above.
A process of preparing a metallic foil backed with a carrier film.
A process of oxidizing the surface suitable for the outside of a metallic foil backed with a carrier film.
A process of transferring a metallic foil on a raw ceramic compact from a carrier film in the state where the surface where a metallic foil oxidized was made to counter a raw ceramic compact.
A process of calcinating a raw ceramic compact by which a metallic foil was transferred in a reducing atmosphere.

[0016]This invention is turned also to a manufacturing method of a lamination type ceramic electronic component again. ******** is characterized by a manufacturing method of a ceramic electronic component comprising the following, in order to solve a technical technical problem mentioned above.
A process of preparing a metallic foil backed with a carrier film.
A process of oxidizing the 1st surface suitable for the outside of a metallic foil backed with a carrier film.
A process of transferring a metallic foil on a ceramic green sheet from a carrier film in the state where the 1st surface was made to counter a ceramic green sheet.
A process of oxidizing the 2nd surface suitable for the outside of a metallic foil transferred on a ceramic green sheet, a process of laminating two or more ceramic green sheets, and producing a raw layered product, and a process of calcinating a raw layered product in a reducing atmosphere.

[0017]As for a metallic foil, in a manufacturing method of such a ceramic electronic component or a lamination type ceramic electronic component, it is preferred that at least one sort chosen from silver, palladium, copper, nickel, molybdenum, tungsten, and tin is included.
[0018]In preparing a metallic foil backed with a carrier film, it is preferred to form a metallic foil with plating on a carrier film.
[0019]In oxidizing the surface of a metallic foil, it is preferred to heat-treat a metallic foil in

adjusted atmosphere.
[0020]When the surface of a metallic foil is oxidized, an oxide film is formed on the surface of a metallic foil, but as for thickness of this oxide film, it is preferred to be chosen as the range of 0.01-30 micrometers.
[0021]As for a raw ceramic layered product or a ceramic green sheet, it is preferred that a glass component is included.
[0022]It is preferred to have further a process of patterning a metallic foil backed with a carrier film by etching before a process of transferring a metallic foil.
[0023]This invention is turned also to a ceramic electronic component obtained again by a manufacturing method which was mentioned above, or a lamination type ceramic electronic component.
[0024]
[Embodiment of the Invention]Drawing 1 and drawing 2 are the sectional views showing the typical process included in the manufacturing method of the lamination type ceramic electronic component by one embodiment of this invention one by one.
[0025]First, as shown in drawing 1 (1), the metallic foil 2 backed with the carrier film 1 is prepared.
[0026]It has the heat resistance which has flexibility, for example, does not change at the temperature of about 100 ** as construction material of the carrier film 1 mentioned above, and what can fully be borne also to plating or vacuum evaporation is used. As an example, the carrier film 1 which consists of polyethylene terephthalate is used advantageously.
[0027]The metallic foil 2 is given, for example by copper foil. As for such a metallic foil 2, being formed by plating is preferred.
[0028]The metallic foil 2 is patterned by carrying out an etching process, after carrying out the coat of the resist to the metallic foil 2 and performing exposure and development based on a photolithography, for example, in order to obtain the pattern of the conductor film needed in the lamination type ceramic electronic component made profitably like. The metallic foil 2 shown in drawing 1 (1) is in the state after such patterning.
[0029]Next, as shown in drawing 1 (2), the 1st surface 3 suitable for the outside of the metallic foil 2 backed with the carrier film 1 oxidizes, and the 1st oxide film 4 is formed of it. It is made for the thickness of this 1st oxide film 4 to serve as the range of 0.01-30 micrometers preferably.
[0030]In performing oxidation treatment mentioned above, the process of, for example, heat-treating the metallic foil 2 in the adjusted atmosphere is carried out. In heat treatment for this oxidation, the thickness of the 1st oxide film 4 mentioned above can be adjusted by changing the oxygen tension which gives atmosphere, introducing a steam, ozone, etc. into atmosphere, or changing the temperature and processing time which are applied in heat treatment. It is

preferred that it is 150 ** or less which modification of the carrier film 1 which consists of polyethylene terephthalate about the temperature of heat treatment does not produce easily.
[0031]With the metal which serves as a passive state by oxidation, like aluminum, concerning the metal which constitutes the metallic foil 2. Since diffusion of oxygen to an inside becomes impossible and oxidation does not advance by forming a very thin oxide film in the surface, it is difficult to form the oxide film which has predetermined thickness.
[0032]On the other hand, since copper oxide has not a passive state but a PORASU rather structure when the metallic foil 2 comprises copper, the oxide film 4 of arbitrary thickness can be easily formed by being able to make an inside diffuse oxygen and managing oxidation treatment conditions. From this viewpoint, what contains tin, silver, palladium, nickel, molybdenum and tungsten, or these metal besides copper as the main ingredients can be advantageously used as metal which constitutes the metallic foil 2.
[0033]Next, as shown in drawing 1 (3), the ceramic green sheet 5 is prepared and the metallic foil 2 is transferred on the ceramic green sheet 5 from the carrier film 1 in the state where the 1st surface 3 of the metallic foil 2 was made to counter this ceramic green sheet 5.
[0034]In the transfer mentioned above, hot stamping to which a suitable pressure and temperature are given, for example is applied.
[0035]As for the ceramic green sheet 5, it is preferred that the charge of a low-temperature-sintering ceramic material which can be calcinated, for example at the temperature of 1000 ** or less is included. At calcination temperature, this charge of a low-temperature-sintering ceramic material contains the glass component used as proper viscosity, and it is preferred that it is in the range with good and wettability with a metallic oxide and solubility proper as such a glass component in which a metallic oxide is dissolved.
[0036]Next, as shown in drawing 2 (1), the 2nd surface 6 suitable for the outside of the metallic foil 2 transferred on the ceramic green sheet 5 oxidizes, and the 2nd oxide film 7 is formed of it. Suppose that it is the same as that of the case of the 1st oxide film 4 mentioned above substantially about the method and conditions for forming this 2nd oxide film 7. As for the thickness, it is preferred also about the 2nd oxide film 7 that it is in the range of 0.01-30 micrometers.
[0037]Next, as shown in drawing 2 (2), two or more ceramic green sheets 5 are laminated, and the raw layered product 8 is produced by it. any of the field where the metallic foil 2 touches the ceramic green sheet 5 in drawing 2 (2) although, as for the raw layered product 8, a part of the laminating direction is only illustrated -- although -- it is given with the oxide film 4 or 7.
[0038]Next, after the raw layered product 8 is pressed in a laminating direction, being heated, it is calcinated in reducing atmosphere through a de binder process.
[0039]In this baking process, the glass component contained in the ceramic green sheet 5 is heated, will be in a hypoviscosity state, permeates each of the oxide films 4 and 7 based on

capillarity, and gets wet and spreads in the oxide film 4 and 7.
[0040]Thus, the glass component which got wet and spread in the oxide film 4 and 7 forms anchor structure between an oxide and a ceramic particle, dissolving some oxides like the copper oxide which constitutes the oxide films 4 and 7. If a glass component arrives at the field side of the oxide films 4 and 7 in the metallic foil 2, and other metal parts, in these interfaces, it will generate a chemical bond and will join firmly the ceramics and the metallic foil 2 by the side of the ceramic green sheet 5 by it.
[0041]When copper is used as metal which constitutes the metallic foil 2, the oxide films 4 and 7 are mainly constituted by Cu_2O, and a chemical bond, such as Cu-Cu-Cu-O-Cu-O-Si-O-, is generated in the interface mentioned above.
[0042]Thus, in order to heighten the junction power of the ceramic layer and the metallic foil 2 which are produced by calcinating the ceramic green sheet 5, the role with the important oxide films 4 and 7 is played. When such an oxide film is not formed, the wettability of the metal and the glass component like copper which constitute the metallic foil 2 is not good, and also since the metallic foil 2 is precise, a glass component does not permeate the metallic foil 2.
[0043]As for each thickness of the oxide films 4 and 7, as mentioned above, it is preferred that it is in the range of 0.01-30 micrometers. If each thickness of the oxide films 4 and 7 becomes thin with less than 0.01 micrometers, a metallic oxide like copper oxide will dissolve altogether substantially into a glass component, The anchor structure in the interface of the oxide films 4 and 7 and a ceramic layer may not be formed, or a chemical bond may not be generated by the interface of the oxide films 4 and 7 in the metallic foil 2, and other metal parts. On the other hand, when the oxide films 4 and 7 become thick exceeding 30 micrometers, a glass component does not permeate the oxide films 4 and 7 whole [each], but the oxide film 4 and the original vulnerable portion of seven may remain as it is in each of the oxide films 4 and 7.
[0044]The embodiment described above tends to be related with the manufacturing method of a lamination type ceramic electronic component, and tends to form an inner conductor layer with the metallic foil 2. Therefore, the ceramic green sheet 5 contacts the both sides of the 1st and 2nd surfaces 3 and 6 of the metallic foil 2, It is necessary to heighten junction power with a ceramic part about these 1st and 2nd surfaces 3 and 6, and he is trying to form the 1st and 2nd oxide films 4 and 7 along these 1st and 2nd surfaces 3 and 6 so, respectively.
[0045]However, when a metallic foil contacts a ceramic part only on the one side, it is sufficient if an oxide film is formed only along one surface of a metallic foil. Namely, the conductor film formed on the outside surface of a lamination type ceramic electronic component, Or about the conductor film more generally formed on the outside surface of the ceramic element assemblies with which a ceramic electronic component is equipped, if an oxide film is formed in the side in contact with the ceramic part of the metallic foil which gives these conductor films, it is sufficient.

[0046]After preparing the metallic foil 2 backed with the carrier film 1 as shown in drawing 1 (1) if an above-mentioned thing is explained again with reference to drawing 1, as shown in drawing 1 (2), the surface 3 suitable for the outside of the metallic foil 2 backed with the carrier film 1 is oxidized, and the oxide film 4 is formed.
[0047]Subsequently, as shown in drawing 1 (3), transferring the metallic foil 2 on the raw ceramic compact 5 from the carrier film 1 in the state where the surface 3 where the metallic foil 2 oxidized was made to counter a ceramic green sheet or the raw ceramic compact 5 is performed.
[0048]And a desired ceramic electronic component is obtained through the process of calcinating the raw ceramic compact 5 by which the metallic foil 2 was transferred as mentioned above in a reducing atmosphere.
[0049]In the embodiment mentioned above, in order to give a desired pattern to the metallic foil 2, carried out the process of patterning the metallic foil 2 backed with the carrier film 1 by etching, before the process of forming the 1st oxide film 4 in the 1st surface 3 of the metallic foil 2, but. As long as such a pattern process is a front [process / of transferring the metallic foil 2 to a ceramic green sheet or the raw ceramic compact 5], it may be carried out in which stage. For example, after forming the 1st oxide film 4, or after forming the 2nd oxide film 7, such a pattern process may be carried out.
[0050]After forming the metallic foil 2 on the carrier film 1, patterning of the metallic foil 2 is not performed, but it is a stage which forms the metallic foil 2 on the carrier film 1, and may be made to form the metallic foil 2 patterned beforehand, for example using a mask. In the process of transferring the metallic foil 2 to a ceramic green sheet or the raw ceramic compact 5, as only the predetermined portion of the metallic foil 2 is transferred selectively, it may be made to pattern the metallic foil 2.
[0051]Below, the example of an experiment carried out in order to check the effect by this invention is explained.
[0052]
[Example(s) of Experiment]After preparing the carrier film which consists of polyethylene terephthalate, on the other hand performing catalyst grant and activation, chemical plating was carried out for 4 minutes by 80 ** of solution temperature, and the metallic foil which consists of 5-micrometer-thick copper was formed.
[0053]Subsequently, the coat of the resist was carried out to this metallic foil, the exposure and development by a photolithography were performed, the aqua fortis performed etching for 2 seconds, and the metallic foil was patterned.
[0054]Subsequently, the metallic foil which consists of copper patterned in this way was heat-treated for 20 minutes at the temperature of 80 ** in an air atmosphere by the state where it was backed with the carrier film. By this, the oxide film of about 0.8 micrometer average

thickness was formed in the surface suitable for the outside of a metallic foil. Although the main ingredients of this oxide film were Cu_2O, metallic copper and CuO were also detected.

[0055]Next, the metallic foil was transferred on the ceramic green sheet from the carrier film in the state where the surface in which the oxide film of the metallic foil was formed was made to counter a ceramic green sheet. Here, the thing containing the charge of a low-temperature-sintering ceramic material containing 50 % of the weight of alumina and 50 % of the weight of aluminum-Si-Ba-Sr-B-O system glass was used as a ceramic green sheet. Hot stamping was applied when transferring and the pressure of 100kg[/cm] ^{2} and the temperature of 100 ** were given for 10 seconds in this hot stamping.

[0056]Next, it oxidized by the conditions which mentioned above the surface suitable for the outside of the metallic foil transferred on the ceramic green sheet, and the same conditions, and the oxide film was formed even if it met this surface.

[0057]Subsequently, the raw layered product obtained by laminating two or more ceramic green sheets which have the metallic foil which forms the oxide film in each of the surface which carries out for relativity as mentioned above was pressed for 45 seconds by the temperature of 80 **, and the pressure of 1000 t/cm^2.

[0058]Subsequently, after carrying out debinding processing of the raw layered product after this press, in the reducing atmosphere, it calcinated at the temperature of 950 **, and the multilayered ceramic substrate was produced.

[0059]Thus, about the multilayered ceramic substrate concerning the obtained sample, the bonding strength of the metallic foil and ceramic part which were measured by the friction test became 1.9 kgf/cm^2.

[0060]On the other hand, in the multilayered ceramic substrate pass the operation mentioned above except for not forming an oxide film as a comparative example, and the same operation, the bonding strength of a metallic foil and a ceramic part was only 0.4 kgf/cm^2.

[0061]

[Effect of the Invention]As mentioned above, by oxidizing the surface which touches the ceramic part of this metallic foil, using a metallic foil as a conductor film in manufacturing a ceramic electronic component or a lamination type ceramic electronic component according to this invention, Since the oxide film is formed, the bonding strength of a ceramic part and a metallic foil can be raised.

[0062]According to this invention, in a ceramic electronic component or a lamination type ceramic electronic component, since the conductor film is formed with the metallic foil, compared with the case where conductive paste is used, lamination of a conductor film, improvement of a high frequency characteristic, and micrifying of a pattern can be attained.

[0063]In this invention, since it will not become a passive state by oxidation if at least one sort

chosen from silver, palladium, copper, nickel, molybdenum, tungsten, and tin is used as metal which constitutes a metallic foil, the oxide film of desired thickness can be formed easily.
[0064]In this invention, if a metallic foil is formed with plating, compared with other thin film processes, such as sputtering, it will become possible to form a metallic foil by low cost.
[0065]In this invention, if the surface of a metallic foil is faced oxidizing and a metallic foil is heat-treated in the adjusted atmosphere, the thickness of the oxide film formed on the surface of a metallic foil is easily controllable.
[0066]If this is chosen as the range of 0.01-30 micrometers about the thickness of the oxide film mentioned above, a firm jointing condition can be more certainly acquired between a metallic foil and a ceramic part.
[0067]When a raw ceramic layered product contains a glass component especially, this glass component permeates an oxide film, the anchor structure and the chemical bond by a glass component are formed, and the bonding strength of a ceramic part and a metallic foil can be raised more.
[0068]If the metallic foil backed with the carrier film is patterned by etching in this invention before the process of transferring a metallic foil to a raw ceramic compact or ceramic green sheet, While being able to pattern efficiently, a minute pattern can be easily given to a metallic foil.

[Translation done.]